

**LEVELS OF CHLORINATED ORGANICS  
IN A MUNICIPAL INCINERATOR**

**R. E. Clement, H. M. Tosine and J. Osborne  
Ontario Ministry of the Environment  
Laboratory Services and Applied Research Branch  
P.O. Box 213, (Resources Road)  
Rexdale, Ontario, Canada M9W 5L1**

and

**V. Ozvacic and G. Wong  
Ontario Ministry of the Environment  
Air Resources Branch  
880 Bay Street, 4th Floor  
Toronto, Ontario, Canada M5S 1Z8**

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## INTRODUCTION

The presence of polychlorinated dibenzo-p-dioxins (PCDD) in emissions from municipal incinerators is well documented in a review by Lustenhouwer (1). Municipal incinerators in The Netherlands, Canada, Japan, Switzerland, Italy, Germany, France, Sweden, and the United States have been studied. In spite of the many designs of these incinerators, and the variation in composition of municipal waste that exists among the different countries, PCDD has been detected in all studies. Large differences, however, exist in the relative amounts of various PCDD congeners and in the pattern of isomers within each specific congener, for samples taken from different incinerators.

Although they have not yet been as fully investigated as the PCDD compounds, the polychlorinated dibenzofurans (PCDF) are also prominent in municipal incinerator emissions. In fact, total PCDF concentrations are generally greater than total PCDD concentrations. The emphasis of some investigations on levels of PCDD is a result of the great concern over one specific compound, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Isomer-specific analysis for this compound, however, generally has shown it is a minor component of the total concentration of tetrachlorinated dibenzo-p-dioxins (2). Since several of the PCDF compounds have demonstrated similar toxicities to the toxicity of 2,3,7,8-TCDD in laboratory animal studies, estimates of the environmental impact of incinerator emissions must take into account PCDF as well as PCDD levels.

Laboratory studies have shown that PCDD/PCDF compounds can be formed in chemical reactions involving such precursors as chlorinated phenols (3), chlorobenzenes (4), and polychlorinated biphenyls (5). Although it has not been demonstrated that the mechanisms of PCDD/PCDF formation in incinerators involve these precursors, a recent study has shown them to be present in large quantities in the emissions of a municipal incinerator situated in the United States (6). By monitoring levels of possible precursors in addition to levels of PCDD/PCDF compounds, an indication of the mechanism for PCDD/PCDF formation may be established. The chemistry of combustion reactions which occur in municipal incinerators is so complex that this indirect approach is necessary.

The principal variables which affect PCDD/PCDF formation must be associated with the composition of the feedstock and the incinerator operating conditions. No investigations of these factors have yet been reported. Such studies may indicate methods of reducing the formation of PCDD/PCDF compounds.

The data presented in this chapter are the first to include levels of chlorinated compounds in the feedstock to, as well as in the emissions from, a municipal incinerator. Possible precursors such as chlorophenols, chlorobenzenes and polychlorinated biphenyls have been measured in addition to the various PCDD and PCDF congeners. Furthermore, all solid and liquid process sidestreams and stack emissions were analyzed, to give a total picture of incinerator emissions.

## EXPERIMENTAL

### Collection of Samples

#### Description of Facility

Figure 1 is a simplified diagram of the municipal incinerator studied. The overall facility consists of three incinerators, each with its own cooling tower and electrostatic precipitator, that feed into a common stack. The incinerators are not designed for energy recovery. Refuse is charged to the feed chute at a rate of approximately 8 metric tons/hour per incinerator. The refuse is incinerated at a temperature of  $1010^{\circ}\text{C}$ . Extraneous heating of the burning garbage is usually not required, but is added by two natural gas burners when the temperature of the furnace exit gases falls below  $870^{\circ}\text{C}$ . Heavy ash falls through the grates to hoppers which in turn discharge the ash to a water filled trough. Trough effluent is discharged via an overflow pipe which is fed to sanitary sewers. Samples of this trough overflow water and particulates in the trough overflow water were collected for analysis. The ash from the trough is transported by conveyors to a holding area. This holding area includes bottom ash, precipitator fly-ash, particulates from the cooling tower, and scrubber particulates. The particulates in the holding area, which are used for landfill, are called combined ash. The amount of fly ash in the combined ash is unspecified but is probably no greater than 2 to 4% of the combined ash by weight. The bottom ash was inaccessible for sampling before being mixed with fly-ash. A cooling tower is needed to reduce the temperature of incinerator gases from about  $900^{\circ}\text{C}$  to  $280^{\circ}\text{C}$ . About 50% of the cooling tower water used for this purpose is vaporized and eventually emitted from the stack. Temperatures in the stack range from about  $230^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ .

and stack gas velocities are  $1.5 \text{ ms}^{-1}$  to  $8.2 \text{ ms}^{-1}$ . Stack gas moisture content is over 30%.

### Stack Sample Collection

Three 24-hour stack samples were collected in a 1-week time period during December, 1981, using a modified EPA Method 5 train. Changes to the EPA train are shown in Figure 2. After the third impinger, two florisil cartridges were placed in series. The cartridges were each packed with about 10 grams of florisil, and were held in place vertically to avoid channelling. Volumes of gas collected (dry reference) in the three 24-hour tests were 15.4, 16.2 and 16.9 cubic metres. The weights of particulate matter collected on corresponding filters were 240, 514 and 784 mg. Each stack sample collected resulted in 4 samples for GC-MS analysis including the filter and rinsings from the probe and front part of the sampling train, impinger contents and rinsings, and two separate florisil cartridges. Figure 1 shows the location of the stack sampling ports.

### Process Sample Collection

Process samples refer to solid material including combined ash, dry precipitator fly-ash, particulates from the trough overflow water and cooling tower effluent, and liquid samples which include the trough overflow and cooling tower effluent. One set of process samples was collected for each stack sample. To obtain samples which were representative of the stack sample, each process sample was taken every 3 hours from each incinerator during the 24-hour stack sampling period. For



each type of sample, the separate 3-hour samples were combined and well mixed to give a 24-hour composite. Particulate samples were well-ground to increase sample homogeneity. From the composite samples an aliquot of 4 litres (trough overflow water, cooling tower effluent) or 50 grams (particulate samples) was used for extraction and analysis. Incinerator sampling locations for the various process samples are indicated on Figure 1.

#### Feedstock Sampling Procedure

A representative sample, based on visual inspection, of 140 to 180 kg refuse was taken every 3 hours from a pit which holds the refuse charged to each incinerator during the 24-hour stack sampling period. Individual 3-hour samples were sorted into four categories: paper products, wood products and textiles; plastics, rubber and leather products; food and gardening wastes; and ferrous metal, non-ferrous metal and glass products. The weights of these different fractions were recorded and a composite sample of about 10 kg containing the categories in their correct weight ratios was obtained. Individual 3-hour samples of material from the first three categories were shredded together to produce a 24-hour composite sample. The shredded composite sample was then milled to less than 0.5 mm. Fifty grams of this sample were extracted as described later. The ferrous and non-ferrous fractions of the 3-hour samples were not milled or extracted.

## Extraction of Samples

### Spiking of Samples

To evaluate the efficiency of extraction, cleanup and GC-MS analysis of samples, a known amount of  $^{37}\text{Cl}$ -octachlorodibenzo-p-dioxin ( $^{37}\text{Cl}$ -OCDD) was added to each sample prior to extraction. Stack samples were recovered from the sampling train before spiking. Quantification of the amount of spike recovered was performed by GC-MS.

### Stack Sampling Train Extraction

#### Sampling Probe, Nozzle, Front Half of Filter Holder, Cyclone Bypass.

Stack sampling trains were transported intact to the laboratory. All openings were sealed with aluminum foil prior to transport. The interior of the probe was rinsed 3 x with pentane, then brushed with a precleaned shotgun brush under additional pentane washing. The brush was rinsed with pentane to collect any trapped particulates, then the entire rinsing procedure was repeated using methylene chloride. The nickel plated nozzle and glassware from the front half of the train were each rinsed twice with pentane and methylene chloride. Rinsings were filtered through the train's spent glass fibre filter and retained for subsequent Soxhlet extraction of the filtered particulates.

Glass Fibre Filter Extraction. After drying at ambient temperature and weighing to determine the particulate catch, the filter and residue were ground using mortar and pestle and stirred with 300 ml of 1 molar HCl for one hour. The residue was centrifuged, filtered using a new glass fibre

filter and rinsed with deionized water. The filter and residue were then air dried and extracted in a Soxhlet apparatus. Pentane and methylene chloride rinses from the front half of the sampling probe were used initially as extraction solvents, at a cycle rate of 3 per hour for 8 hours. A second 24-hour extraction was performed using toluene. The samples were charged to glass extraction thimbles for these extractions over a bed of pre-extracted silica (5 to 15 grams, depending on sample size). After column chromatography clean-up, final sample volume for GC-MS analysis was 10  $\mu$ l.

Impinger Contents and Associated Glassware. The glass fibre filter-glass fritted support was extracted with 2 x 300 ml pentane and then 2 x 300 ml methylene chloride in an ultrasonic bath. Pentane and methylene chloride rinses of the rear half of the filter holder were added to the respective pentane and methylene chloride filter frit extracts. Impinger connecting glassware was rinsed with small volumes of acetone, followed by 4 x rinsings employing generous quantities of pentane, and methylene chloride. The pentane and acetone rinses of connecting glassware were added to the pentane extract of the glass fritted filter support, while the methylene chloride extract was added to the corresponding methylene chloride extract of the glass fritted filter support.

Liquid-liquid extraction of impinger contents was performed using the acetone/pentane rinse described above, with the addition of sufficient pentane to ensure a total extraction volume of 300 ml solvent per litre of impinger solution.

Extraction was repeated 4 times by vigorous shaking for at least 5 minutes each time, and each extract was filtered through precleaned anhydrous sodium sulphate. The above procedure was repeated using methylene chloride. Extracts were concentrated by a Kuderna-Danish evaporator, cleaned-up by column chromatography, and combined to a final sample volume of 50 ul for GC-MS analysis.

Florisil Cartridges. Florisil cartridge contents were extracted using about 150 ml pentane/methylene chloride by Soxhlet apparatus. Eight hour extraction periods with a cycle rate of 3 per hour were employed. Soxhlet extraction was repeated for an additional 8-hours using toluene. Extracts were concentrated by Kuderna-Danish apparatus, cleaned-up as described later, and combined for GC-MS analysis. Final sample volume for analysis of florisil extracts was 10 ul.

#### Process Sample Extraction

Liquid Samples Including Trough Overflow and Cooling Tower Effluent. A four-litre aliquot of the 24-hour composite was extracted using a separatory funnel and employing 300 ml pentane per litre of sample. Each pentane extract was filtered through anhydrous sodium sulphate. The entire extraction procedure was repeated with methylene chloride. Extracts were concentrated by Kuderna-Danish for column chromatography clean-up. Final sample volume for GC-MS analysis was 10 ul.

Solid Samples Including Precipitator Fly Ash, Combined Ash, Filtered Residues from Liquid Samples, Feedstock. For fly-ash, combined ash, and feedstock, 50 g aliquots of the 24-hour composite were used for Soxhlet extraction. Before extraction, acid treatment of particulates was performed using 1M HCl as described for the glass fibre filter. Extraction was by Soxhlet apparatus for 48 hours using toluene. After column chromatography cleanup, extracts were reduced to 100 ul (fly-ash) or 10 ul (other particulate samples) for GC-MS analysis. All samples were spiked with  $^{37}\text{Cl}$ -OCDD before extraction.

#### Glassware Preparation

All glassware was cleaned by washing with aqueous detergent solution, rinsing with tap and distilled water, then by multiple solvent rinsings using methanol, acetone and methylene chloride. A final pentane rinse was collected, concentrated by Kuderna-Danish apparatus, and then analyzed by GC-electron capture detection. Solvent rinsing of glassware was repeated if necessary until the GC analysis showed no peaks were present in the PCDD/PCDF elution region. All solvents were distilled-in-glass grade from Caledon Laboratories, Georgetown, Ontario, Canada.

#### Column Chromatography Cleanup

The initial cleanup column consisted of, from bottom to top of column, 1.0 g silica, 2.0 g of 33% 1M NaOH on silica, 1.0 g silica, 4.0 g of 44%  $\text{H}_2\text{SO}_4$  on silica, and 2.0 g silica. After a pre-wash with 30 ml hexane, incinerator samples were charged to the top of the column with 3 x 5 ml

hexane rinses of the sample container, and eluted with an additional 85 ml hexane. A keeper of 0.5 ml isooctane was added to the effluent, which was then concentrated to about 5 ml. The packing material retained chlorophenols (CP), which were extracted by shaking with hexane and methylene chloride. Chlorophenol extracts were concentrated by Kuderna-Danish apparatus and methylated for analysis by gas chromatography.

The concentrated eluant from the initial cleanup column was further treated using a dual-column system consisting of a short top column of 10%  $\text{AgNO}_3$  on silica and a bottom alumina column. Samples were eluted using 100 ml pentane, which was collected for polychlorinated biphenyl (PCB) and chlorobenzene (CB) analysis. Before GC analysis, the pentane extract containing PCB and CB compounds was concentrated by Kuderna-Danish apparatus and eluted through a 16 cm florisil column using 20 ml of pentane.

After eluting PCB and CB compounds from the dual-column system, the top  $\text{AgNO}_3$  column was removed and the alumina column rinsed with 20 ml of 10%  $\text{CCl}_4$  in hexane followed by 20 ml hexane. PCDD and PCDF compounds were then recovered from the alumina by elution with 45 ml methylene chloride. Final sample volumes for GC-MS analysis were 10 ul to 100 ul in isooctane solvent. Final sample volumes were achieved by evaporating to dryness in Pierce reacti-vials and adding the appropriate solvent volume by microlitre syringe.

## Instrumental Analysis

### PCDD/PCDF Determination

Concentrated sample extracts were analyzed by capillary column GC-low resolution MS. A fused silica column (30 m x 0.22 mm, J + W Scientific) was directly coupled to the ion source of a Finnigan 4000 GC-MS equipped with INCOS data system. Splitless injection was employed, and the GC was programmed from 80°C to 235°C at 15°C/min., then to 280°C at 4°C/min., and held at 280°C for 10 min. Injection temperature was 260°C and the GC-MS transfer line was 280°C.

Analysis was performed by operating the MS in the selected ion monitoring (SIM) mode. Three ions were monitored for each PCDD and PCDF congener, corresponding to the  $M^+$ ,  $(M + 2)^+$  and  $(M + 4)^+$  ions. For maximum sensitivity, only 6 ions were monitored at a time, for the PCDD and PCDF compounds having the same number of chlorine atoms. This group of 6 ions was switched at previously determined times, just before the compounds of the next higher degree of chlorination started to elute from the GC column. Separation between PCDD/PCDF compounds containing different degrees of chlorination was sufficient to allow detection of all PCDD and PCDF compounds containing four or more chlorines. No attempt was made to determine lower chlorinated PCDD/PCDF compounds.

Quantification was by an external standard which contained 1,2,3,4-TCDD, 2,3,7,8-TCDD, 2,3,7,8-TCDF, one representative isomer of the penta, hexa and heptachlorinated dibenzo-p-dioxins, octachlorodibenzo-p-dioxin (OCDD), and octachlorodibenzofuran (OCDF). Concentrations of compounds in the external standard ranged from 30 to 40 picograms/ul. PCDD and PCDF data were not corrected for recovery of the internal spike.

#### Chlorophenols (CP), Chlorobenzenes (CB), Polychlorinated Biphenyls (PCB)

##### Determination

CP, CB and PCB analyses were performed by dual capillary column gas chromatography-dual electron capture detector (ECD). A Varian 6000/Vista 402 GC was equipped with two 50 m x 0.2 mm fused silica columns, one an SE54 phase and the other an OV-1 phase. The GC oven was programmed from 90°C to 260°C at 3°C/min., and held for 3 min. Identification of CP, CB and PCB peaks was by correspondence of retention times on the two columns with those of standards. Also, the ratio of peak areas from each compound on the two ECD detectors was required to match the ratio determined by injection of an external standard. Quantification was based on this external standard mixture which contained all CP and CB compounds.

#### RESULTS AND DISCUSSION

Table I is a list of the samples analyzed, and gives amounts extracted as well as some sampling information. Because liquid process samples were expected to be very low in organics content, only one representative sample from the three Tests, of each of these types was



analyzed. No PCDD/PCDF compounds were detected in the trough overflow water, cooling tower water, or quench water; and PCB, chlorophenol, and chlorobenzene amounts were about the same as background levels in these samples. Therefore, remaining liquid process samples were not analyzed.

#### Analytical Results - PCDD and PCDF

In all three Tests, more than 95% of the total PCDD/PCDF detected in train samples was found in the impingers. In process samples, 95% of the total was from the precipitator fly-ash. Figure 3 is a comparison of the total ion plots for the Test 3 impinger and fly-ash extracts. Elution regions for the various PCDD/PCDF congeners are indicated.

A total of thirty ions were required for each PCDD/PCDF analysis, but only 6 were monitored at any specific time. A new group of 6 ions was chosen at the end of each congener elution region indicated in Figure 3. Numbers at the tops of peaks are scan numbers, where each scan consists of the abundances of the six ions monitored. Including the ion dwell times and computer overhead time, each scan required about 1.3 seconds to perform.

#### PCDD/PCDF Isomer Patterns

Patterns of isomers detected for the various PCDD/PCDF congeners varied little between the different types of samples analyzed or from Test-to-Test. Typical patterns are illustrated in Figure 4 for the tetra-, penta-, and hexachlorinated dioxins. Figure 5 shows the

corresponding PCDF isomer patterns. The ion abundance plots in Figures 4 and 5 are from the same fly-ash extract for which the total ion plot is given in Figure 3. Some differences were observed in isomer patterns between samples, but these were generally very small. Figure 6 illustrates the extent of variation in patterns that was observed. In the top two plots of the ion abundance of T<sub>4</sub>CDD from analysis of the Test 1 fly-ash and Test 3 impinger, some differences are evident. The later eluting peaks of the impinger extract are more prominent, relative to the first two peaks. The general patterns, however, are similar and the same isomers observed in the fly-ash extract are present in the impinger extract. For the P<sub>5</sub>CDD analyses shown in the bottom two plots the patterns are more similar. This closer similarity was more often observed in the extracts analysed. No variations in patterns of isomers for specific congeners due to different types of samples or for different Tests were observed.

Figures 4 to 6 also illustrate the low background which was generally observed. Only one of the three ions monitored for each congener has been plotted. Figure 7 is an example of all three ions monitored for the P<sub>5</sub>CDD compounds detected in a precipitator fly-ash extract. All peaks detected are present in all three plots with ratios of 62: 100: 60 for the 354: 356: 358 ions. The theoretical ratios are 61: 100: 65. Figure 7 is typical of sample extracts containing large quantities of PCDD/PCDF. As the amounts detected approach detection limits, the patterns appear to change and the difference between observed and theoretical ratios becomes greater. Data such as illustrated in Figure 7 are a result of the combined use of specific cleanup procedures and selective GC-MS detection.

About 60% of the total possible PCDD/PCDF congeners containing 4 to 8 chlorines were detected as distinct or merged peaks. Table II summarizes the maximum numbers of isomers observed for each congener group. Of the possible 136 different compounds, 81 were observed. For the T<sub>4</sub>CDD, T<sub>4</sub>CDF and P<sub>5</sub>CDF congeners, where the total possible number of isomers is greater than 20 for each group, only 42 of 88 possible compounds were observed, or 48%. In the remaining congeners, 41 of 48 possible compounds, or 85% were observed. This probably indicates that GC resolution is the limitation in observing more isomers. The true number of PCDD/PCDF compounds present is probably greater than 42.

#### Train Sample Data

Results from the analysis of filtered particulates, impingers, and florisil cartridges are shown in Table III. Florisil cartridges were extracted separately but combined before GC-MS analysis. Data from other Ontario Ministry of the Environment studies have shown that the second florisil cartridge contains about 5%, on average, of the PCDD/PCDF detected in the first cartridge (7). The second trap is necessary as a backup in occasional instances where channelling or breakthrough occurs in the first trap.

Data presented in Table III were not adjusted for volumes of stack gases sampled or weight of stack particulates collected. Since all three Tests were conducted for the same sampling period, these data are the amounts of PCDD/PCDF emitted from the incinerator stack during 24 hours. All stack data reported here are compared on this basis.

For the three Tests, an average of only 0.3% of the total PCDD/PCDF was found in the florisil cartridges. In Tests 1 and 3, over 95% of the total was in the impingers, while for Test 2 the total was distributed in a ratio of about 40:60 between the filter and impingers, respectively. Except for the PCDF congeners in Test 3, the amounts detected for various PCDD and PCDF congeners followed the same pattern. This is shown in Table IV, which gives relative congener distributions of PCDD and PCDF in the stack emissions. The most abundant congeners are the hexachlorinated compounds, for both PCDD and PCDF. With a single exception, the octachlorinated species are least abundant, followed by the tetrachlorinated compounds. On average, the hexachlorinated species were 45% of the total PCDD detected in stack emissions, and 30% of the PCDF. Tetrachlorinated isomers only represented 7% of the total PCDD detected. Tetrachlorinated furans averaged 28% of total PCDF detected, but this is due to Test 3, where the PCDF congeners did not follow the same pattern as was observed for the other Tests in which TCDF isomers were only 13% of the total. Total PCDD and total PCDF were about the same for Tests 1 and 2. In Test 3, high levels of TCDF and P<sub>5</sub>CDF congeners account for a total PCDF which is about twice as great as the total PCDD.

#### Process Sample Data

Liquid process samples which were analyzed did not contain detectable amounts of PCDD/PCDF compounds. Data from solid process samples, which include precipitator fly-ash, combined ash and particulates from the trough overflow, are presented in Table V. These data are

presented as total nanograms per gram extracted. No PCDD/PCDF were detected in combined ash samples for Tests 1 and 3. Total PCDD/PCDF found in the Test 2 combined ash extract was only 7% of the total detected in the Test 2 fly-ash extract. About 2 to 4% of weight of the combined ash is from precipitator fly-ash, but the exact amount cannot be specified for the specific incinerator investigated. The remaining weight of combined ash is from bottom ash that falls beneath the grills where initial burning of municipal waste is effected. Data from Table V indicate that bottom ash is not a significant source of PCDD/PCDF compounds. Test 2 combined ash probably contains detectable levels of PCDD/PCDF because it is composed of a much greater fraction of fly-ash than does the Test 1 and 3 combined ash.

PCDD and PCDF detected in precipitator fly-ash and trough overflow particulates generally follow the same pattern as observed for stack emissions, where the hexachlorinated isomers have the highest concentration, compared to the other congeners, and the tetra- and octachlorinated compounds have the lowest relative concentrations. In process sample extracts, the total PCDD concentrations detected were greater than corresponding total PCDF concentrations. This trend, however, was reversed in stack sample extracts, where the average PCDF amounts were greater than average PCDD amounts.

### PCDD/PCDF in Feedstock

Table VI gives the concentrations of PCDD/PCDF detected in the feedstock. No chlorinated dibenzofurans were detected. Lower chlorinated dibenzo-p-dioxins were also not detected. Both H<sub>7</sub>CDD isomers and OCDD were found in feedstock extracts of all three Tests. The concentrations reported are less accurate than for other process samples, because the feedstock extracts contained such high levels of total organics that they were difficult to elute from the cleanup columns employed and required several dilutions before analyzing by GC-MS.

The similar feedstock concentrations for the three Tests reflects the similarity in the composition of the feedstock. Since hand-sorting of raw municipal garbage was required before milling, the approximate component composition of each feedstock sample was determined, and these are presented in Table VII. Test 1 and Test 3 feedstock have virtually identical composition, while Test 2 feedstock has less paper and textiles but more plastics and rubber than do Tests 1 and 3.

### Analytical Results - PCB, CB, CP

#### Train Sample Data

Table VIII is a summary of the polychlorinated biphenyls (PCB), chlorinated benzenes (CB), and chlorophenols (CP) detected in the stack emissions. CB and CP compounds are grouped according to degree of chlorination. As was the case for PCDD/PCDF stack emissions, all data in Table VIII are reported as total nanograms per 24-hour sampling period.

PCB amounts are very low in all samples, compared to CB and CP compounds. The PCB amounts shown in Table VIII are near background levels for filter extracts and not very much greater in the other sample extracts. Over one-half of the total PCB detected in the stack emissions of all three Tests was from the Test 2 impingers, and this amount is low compared to the total CB and CP detected in this sample extract.

The quantities of chlorobenzenes detected on filter extracts were only slightly greater than PCB amounts. Over 99% of total chlorobenzenes were present in the impingers and florasil cartridges. In Test 1, over 90% was in the impingers, but for Test 2 only 40% of chlorobenzenes were in the impingers. Distribution of these compounds between impingers and filters depends upon the filter temperatures, which for all Tests were maintained at about 120°C. These data show that chlorobenzenes in the stack are primarily in the vapour state.

Distribution of CB amounts among the various chlorinated congeners is different for each Test. In Test 1, about 50% of the total CB is from the tetrachlorinated isomers, while for Test 2 the penta- and hexachlorinated compounds are both more abundant, and in Test 3 most of the total CB detected was evenly divided between tetra- and pentachlorobenzene. Of the total chlorobenzenes detected in each Test, the average percent distribution among the tri-, tetra-, penta-, and hexachlorinated compounds was 16: 40: 34: 10. Over 95% of the trichlorobenzenes detected was split about equally between the 1,2,4- and 1,2,3- isomers, while 90% of tetrachlorobenzenes were from the 1,2,4,5- and 1,2,3,4- isomers.

Chlorophenols in stack emissions were trapped efficiently by the impingers, which contained an average of 87% of the total detected in the train sample extracts for the three Tests. Less than 3% of the total was detected in the filter extracts. On average, the total CP quantities in the train were distributed about equally between the tri-, tetra-, and pentachlorinated congeners, which have a percent distribution of the total of 36:40:24, respectively. About 70% of the trichlorinated total was from the 2,4,6-isomer, and 20% was due to the 2,4,5-isomer. For the tetrachlorinated compounds, 93% was from the 2,3,4,6-isomer, while none of the 2,3,5,6-compound was detected.

#### Process Sample Data

Liquid process samples contained very low levels of PCB, CB and CP compounds. In the solid process samples, including precipitator fly-ash, combined ash, and particulates from the trough overflow, only the fly-ash contained appreciable concentrations of CB and CP compounds. PCB were at low concentrations for all process samples, as was observed for the stack samples.

Table IX is a summary of the total PCB, CB, and CP concentrations in process samples. Combined ash and trough overflow particulates contained low concentrations of these compounds, compared to fly-ash and feedstock extracts. It is interesting to note that chlorobenzenes are at 30 x higher concentrations in the fly-ash than the feedstock, chlorophenols are about 2 x higher in fly-ash than feedstock, while PCB concentrations are greater in the feedstock by a factor of 4.



Chlorophenol congener ratios are about the same in fly-ash as for the stack emissions. The percent distribution of total chlorophenols between the tri: tetra: penta chlorinated congeners in the train is 36: 40: 24, respectively, and the corresponding ratios for the precipitator fly-ash are 33: 42: 25. As was observed for the train samples, most of the trichlorinated total was from the 2,4,6-isomer (90%), and the next most abundant trichlorinated phenol was the 2,4,5-isomer (4%). For the tetrachlorinated congeners, the 2,3,5,6-isomer was not detected, while 93% of the total tetra congener amount was contributed by the 2,3,4,6-isomer.

#### Comparison of Chlorinated Species

Three Tests are not sufficient to develop rigorous models to describe the relationships between the various chlorinated species investigated in this study. If such relationships exist, however, then general trends in the data should be evident.

Table X is a comparison in the total PCDD + PCDF, CP and CB levels detected in feedstock, stack, and fly-ash samples for the three Tests. Feedstock and precipitator fly-ash concentrations are ng/g, while the stack values are presented as total nanograms detected during each 24-hour Test. Because PCB levels were generally low and varied little from sample-to-sample or Test-to-Test, they were not included in Table X.

Concentrations of total PCDD/PCDF in feedstock increase stepwise from Test 1 to Test 3 from 0.5 to 1.6 ng/g. This range may not be indicative of real differences in the feedstock concentrations of PCDD/PCDF, considering the difficulties experienced in feedstock analysis. Total stack emissions of PCDD/PCDF for the three Tests,

however, follow the same pattern as feedstock concentrations. By normalizing to the lowest value obtained, relative feedstock concentrations are 1.0:1.8:3.2 for Test 1: Test 2: Test 3, and the corresponding ratios for stack emissions are 1.0:2.2:3.8. Although concentrations in feedstock appear to be very low compared to total stack emissions, it must be remembered that many tons of feedstock were incinerated, and these low concentrations may represent large amounts of PCDD/PCDF input to the incinerator. While stack emissions are composed of the full range of PCDD/PCDF congeners from the tetra to octachlorinated species, only hepta and octachlorinated dibenzo-p-dioxins were detected in feedstock. The patterns observed in feedstock and stack samples were not observed for precipitator fly-ash. The lowest total PCDD/PCDF concentrations in fly-ash occurred for Test 3, although concentrations in the feedstock and stack samples were greatest for this Test.

There appears to be no relationship in the quantities of chlorophenols or chlorobenzenes in the feedstock, stack or fly-ash samples. In feedstock extracts, chlorophenols are lowest in Test 2; for stack emissions, Test 3 is lowest; and for fly-ash, Test 1 is lowest. Chlorobenzenes in stack and fly-ash samples are highest in Test 3, but about the same for Test 1 and Test 2 fly-ash, while chlorobenzenes in the Test 1 stack emissions are much greater than the Test 2 emissions.

No definite trends are apparent in the amounts of chlorobenzenes and total PCDD/PCDF detected in the three Tests. In the precipitator fly-ash, concentrations of PCDD/PCDF decrease from Test 1

to Test 3, while chlorobenzene concentrations increase from Test 1 to Test 3. the absolute differences in concentrations between Tests, however, are not great enough to suggest this trend is significant without conducting many more experiments.

A similar trend is observed between the levels of PCDD/PCDF and levels of chlorophenols in the stack emissions. PCDD/PCDF amounts increase from Test 1 to Test 3, while chlorophenols decrease from Test 1 to Test 3. Test 1: Test 2: Test 3 ratios of PCDD/PCDF levels in stack emissions are 1.0: 2.2: 3.8, while the corresponding ratios for chlorophenols are 2.2: 1.3: 1.0.

## CONCLUSIONS

This study is the first to report levels of chlorinated organics in the feedstock to a municipal incinerator. Although no lower chlorinated PCDD compounds and no PCDF compounds were detected in the feedstock, high levels of all chlorinated congeners of PCDD and PCDF from the tetra to octa species were found in the stack emissions and in the precipitator fly-ash. A few general trends between the levels of CP, CB and PCDD/PCDF compounds were observed, although the number of Tests is too small to determine any definite correlations. PCB levels were generally low for all Tests and different types of samples, often approaching background amounts. It may be concluded that PCB compounds are only minor components of the emissions from the incinerator studied, and they probably are not major contributors to the formation of PCDD/PCDF compounds in this incinerator. Almost all of the PCDD/PCDF emitted from the incinerator were detected in the stack emissions and the precipitator fly-ash. Bottom ash is not a significant source of PCDD/PCDF.

A large number of studies have now been reported concerning the levels of PCDD and/or PCDF compounds in incinerator effluents. Results of these studies are difficult to compare, since few of the studies present data for the same range of compounds and sample types. In most cases, the relative amounts of the various chlorinated congeners are greatest for the higher chlorinated species for both PCDD and PCDF classes of compounds. Often, the hexachlorinated congeners have the greatest relative abundances, for stack emissions and precipitator fly-ash. The ratio of total PCDD:PCDF concentrations will generally be greater in fly-ash than in stack emissions, which probably indicates that PCDF compounds have a greater volatility compared to the corresponding PCDD analogues. Another possibility, however, is that different mechanisms exist for the formation or condensation of PCDD/PCDF compounds on precipitator fly-ash than in the stack emissions.

Concentrations of PCDD/PCDF in fly-ash do not follow the same trend as PCDD/PCDF concentrations in the stack emissions.

For the investigation of relationships between the various chlorinated species, more Tests must be performed. Future investigations should analyze PCDF as well as PCDD congeners in stack emissions as well as in corresponding precipitator fly-ash so that different studies can be compared. Many of the published studies to date are difficult to compare with each other because of the general paucity of data presented. By determining the concentrations of chlorophenols and chlorobenzenes in these samples, in addition to the PCDD/PCDF, the additional data needed to determine relationships between the various chlorinated species can be obtained.

#### ACKNOWLEDGEMENTS

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Table I. Sampling information \*

Sampling Parameter	Test 1	Test 2	Test 3
Average Stack Gas Temp ( $^{\circ}\text{C}$ ) <sub>3</sub>	262	256	245
Stack Gas Volume Sampled ( $\text{m}^3$ )	15.4	16.2	16.9
Stack Particulates Sampled (mg)	240	514	784
Impinger Catch (ml)	2490	2340	2215
ESP Fly-Ash Extracted (g)	50	50	50
Combined Ash Extracted (g)	50	50	50
Trough Overflow Water Extracted (litres)	4	4	4
Trough Overflow Particulates Extracted (g)			
Cooling Tower Water Extracted (litres)	4	4	4
Cooling Tower Particulates Extracted (g)			
Quench Water Volume Extracted (litres)	4	4	4
Quench Water Particulates Extracted (g)			

\* in addition to the samples listed, two florisil cartridges were extracted for each Test. Data presented later are for the totals in both florisil cartridges.

Table II. Chlorinated dibenzo-p-dioxins and dibenzofurans - numbers of isomers observed. \*

	Tetra	Penta	Hexa	Hepta	Octa	Total
PCDD	11/22	11/14	7/10	2/2	1/1	32/49
PCDF	17/38	14/28	13/16	4/4	1/1	49/87
Total	28/60	25/42	20/26	6/6	2/2	81/136

\* A/B: A = number of isomers observed; B = total number of possible isomers.



Table III. PCDD/PCDF in Stack Emissions \*

	TEST 1				TEST 2				TEST 3			
	Filter	Impinger	Florisil	Total	Filter	Impinger	Florisil	Total	Filter	Impinger	Florisil	Total
T <sub>4</sub> CDD	11	450	1.0	460	83	450	ND	530	ND	1000	ND	1000
P <sub>5</sub> CDD	44	540	1.0	580	370	460	2.0	830	1.0	2200	ND	2200
H <sub>6</sub> CDD	77	1900	18	2000	2300	2700	ND	5000	83	5400	6.0	5500
H <sub>7</sub> CDD	81	1000	16	1100	1500	1900	18	3400	170	2300	28	2500
OCDD	76	200	6	280	1600	420	4	2000	29	560	22	610
Total	290	4100	41	4400	5900	5900	24	12000	280	12000	56	12000
T <sub>4</sub> CDF	24	870	1.0	900	58	1000	1.0	1100	ND	9900	1.0	9900
P <sub>5</sub> CDF	44	1100	3.0	1100	350	990	ND	1300	ND	5800	1.0	5800
H <sub>6</sub> CDF	53	2500	11	2600	1600	3700	ND	5300	24	4900	21	4900
H <sub>7</sub> CDF	29	1200	5	1200	880	1500	14	2400	23	5000	10	5000
OCDF	12	200	3	220	130	280	2	410	6.2	280	5.0	290
Total	160	5900	23	6000	3000	7500	17	10000	53	26000	38	26000
Total PCDD + PCDF	450	10000	64	10000	8900	13000	41	22000	330	38000	94	38000

\* All data reported as total nanograms per 24-hr. sampling period

nd = not detected; detection limits are - total T<sub>4</sub>CDD, T<sub>4</sub>CDF, P<sub>5</sub>CDD, P<sub>5</sub>CDF: 0.8 ng/sample; total H<sub>6</sub>CDD, H<sub>6</sub>CDF: 3.0 ng per sample  
data are not corrected for recoveries

Table IV. Relative congener distributions of PCDD/PCDF in stack emissions\*

Congener	TEST 1		TEST 2		TEST 3		AVERAGE NG**	
	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF
tetra	20	40	10	20	20	100	660	4000
penta	30	40	20	30	40	60	1200	2700
hexa	100	100	100	100	100	50	4200	4300
hepta	60	50	70	50	50	50	2300	2900
octa	10	8	40	8	10	3	960	310

\*amount of each congener in nanograms normalized to largest = 100 for PCDD and PCDF in each Test

\*\*average nanograms detected for each congener in three Tests

Table V. PCDD/PCDF concentrations in solid process samples \*

congener	TEST 1			TEST 2			TEST 3		
	fly ash	combined ash	trough overflow	fly ash	combined ash	trough overflow	fly ash	combined ash	trough overflow
T <sub>4</sub> CDD	240	nd	2	200	14	1	64	nd	10
P <sub>5</sub> CDD	600	nd	6	420	41	3	110	nd	23
H <sub>6</sub> CDD	2000	nd	31	1900	57	5	430	nd	70
H <sub>7</sub> CDD	830	nd	20	1200	34	2	190	nd	34
OCDD	140	nd	16	1200	7	2	36	nd	5
Total	3800	nd	75	4900	150	13	830	nd	140
T <sub>4</sub> CDF	150	nd	1	50	3	1	26	nd	26
P <sub>5</sub> CDF	390	nd	6	150	13	1	52	nd	23
H <sub>6</sub> CDF	880	nd	20	680	8	2	120	nd	48
H <sub>7</sub> CDF	350	nd	10	380	17	nd	72	nd	6
OCDF	31	nd	1	62	1	1	8	nd	2
Total	1800	nd	38	1300	42	4	280	nd	110
Total PCDD & PCDF	5600	nd	110	6200	190	17	1100	nd	250

\*All data given as ng/g

nd = not detected;

detection limits are - total T<sub>4</sub>CDD, T<sub>4</sub>CDF, P<sub>5</sub>CDD, P<sub>5</sub>CDF: 0.2 ng/g; total H<sub>6</sub>CDD, H<sub>6</sub>CDF: 1.0 ng/g;

total H<sub>7</sub>CDD, H<sub>7</sub>CDF, OCDD, OCDF: 0.8 ng/g

Table VI. PCDD/PCDF concentrations in feedstock (ng/g)

	Total PCDF	Chlorinated Dioxins					
		Tetra	Penta	Hexa	Hepta	Octa	Total
TEST 1	nd	nd	nd	nd	0.1	0.4	0.5
TEST 2	nd	nd	nd	nd	0.4	0.5	0.9
TEST 3	nd	nd	nd	nd	1.0	0.6	1.6

nd = not detected;

detection limits are - total T<sub>4</sub>CDD, T<sub>4</sub>CDF, P<sub>5</sub>CDD, P<sub>5</sub>CDF: 0.1 ng/g;

total H<sub>6</sub>CDD, H<sub>6</sub>CDF: 0.5 ng/g; total H<sub>7</sub>CDF, OCDF: 0.3 ng/g

Table VII. Approximate feedstock composition \*

	Paper and Textiles	Plastics and Rubber	Garden and Food	Metals and Glass
TEST 1	59	11	17	13
TEST 2	50	18	19	13
TEST 3	59	11	11	19

\* percent of total weight for each type of material

Table VIII. PCB, CB, CP levels in stack emissions \*

	TEST 1				TEST 2				TEST 3			
	Filter	Impinger	Florisil	Total	Filter	Impinger	Florisil	Total	Filter	Impinger	Florisil	Total
Total PCB	48	270	130	450	27	1300	11	1300	nd	**	190	190
Chlorinated Benzenes												
tri	25	920	9300	10000	40	420	5600	6100	37	**	11000	11000
tetra	47	700	28000	29000	68	1300	410	1800	56	**	37000	37000
penta	11	1100	16000	17000	64	3300	220	3600	17	**	37000	37000
hexa	28	1100	400	5100	110	3600	94	3800	11	**	9700	9700
total	110	3800	58000	62000	280	8700	6300	15000	120	**	95000	95000
Chlorinated Phenols												
tri	6100	52000	7300	65000	nd	28000	2200	30000	650	5600	2700	9000
tetra	nd	35000	7500	43000	nd	29000	50	29000	nd	36000	920	37000
penta	50	18000	4500	23000	nd	23000	880	24000	90	18000	880	19000
total	6200	110000	19000	140000	nd	80000	2300	82000	740	60000	4500	65000
total PCB, CB & CP	6400	114000	77000	200000	310	90000	8600	98000	860	60000	100000	160000

\*Total nanograms in 24-hour stack sample

\*\*Sample lost in preparation

nd = not detected;

detection limits for total PCB: 2.0 ng; total trichlorophenols: 20 ng/sample; total tetrachlorophenols and pentachlorophenol: 10 ng/sample

Table IX. Total concentrations of PCB, CB, CP in process samples \*

	Fly-ash			Feedstock			Combined Ash			Trough Overflow		
	1	2	3	1	2	3	1	2	3	1	2	3
PCB	24	360	54	110	1500	250	2	7	3	1	nd	1
CB	1000	1100	2400	35	42	47	17	26	30	1	1	1
CP	400	760	1100	400	84	470	10	1	10	5	4	6
Total	1400	2200	3600	550	1600	770	29	34	43	6	5	7

\*all concentrations in ng/g  
 nd = not detected  
 1,2,3 = Test 1, Test 2, Test 3

Table X. Comparison of chlorinated organics in incinerator samples \*

	Total PCDD + PCDF			Total Chlorophenols			Total Chlorobenzenes		
	1	2	3	1	2	3	1	2	3
Feedstock	0.5	0.9	1.6	400	84	470	35	42	47
Stack	10000	22000	38000	140000	82000	65000	62000	15000	95000**
Fly-Ash	5600	6200	1100	400	760	1100	1000	1100	2400

\* Feedstock and fly-ash total concentrations in ng/g; stack emissions are total ng detected in each 24-hour Test

\*\*Does not include contribution from impingers

1,2,3 = Test 1, Test 2, Test 3



## FIGURE CAPTIONS

- Figure 1. Simplified diagram of municipal incinerator.
- Figure 2. Modified EPA Method 5 train used to sample stack emissions.
- Figure 3. Total PCDD/PCDF ion plot for Test 3 impinger and fly-ash extracts.
- Figure 4. Isomer patterns for tetra, penta and hexachlorinated dibenzo-p-dioxins from GC-MS analysis of fly-ash extract.
- Figure 5. Isomer patterns for tetra, penta and hexachlorinated furans from GC-MS analysis of fly-ash extract.
- Figure 6. Comparison of tetra and pentachlorinated dibenzo-p-dioxins from GC-MS analysis of Test 1 fly-ash and Test 3 impinger extracts.
- Figure 7. Correspondence of 3 ions for GC-MS analysis of pentachlorinated dibenzo-p-dioxins in fly-ash extract.

Figure 1: clement et al

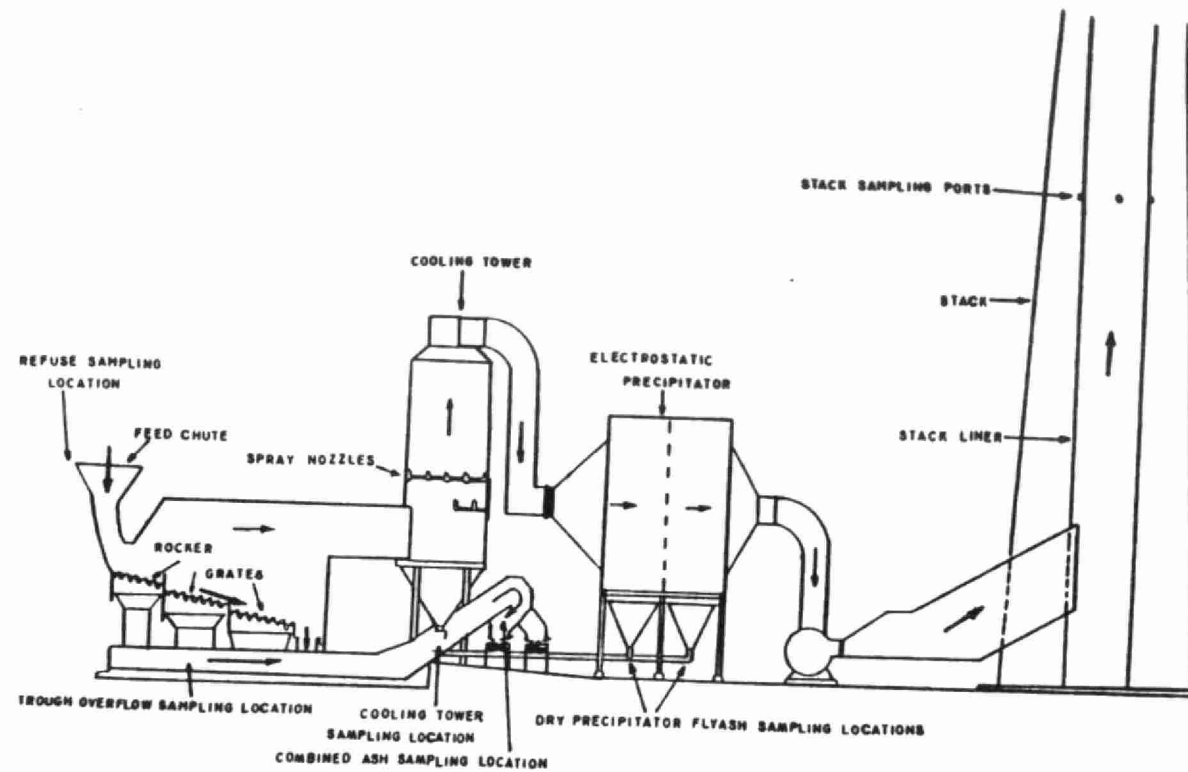


Figure 2 - Chabot  
et al

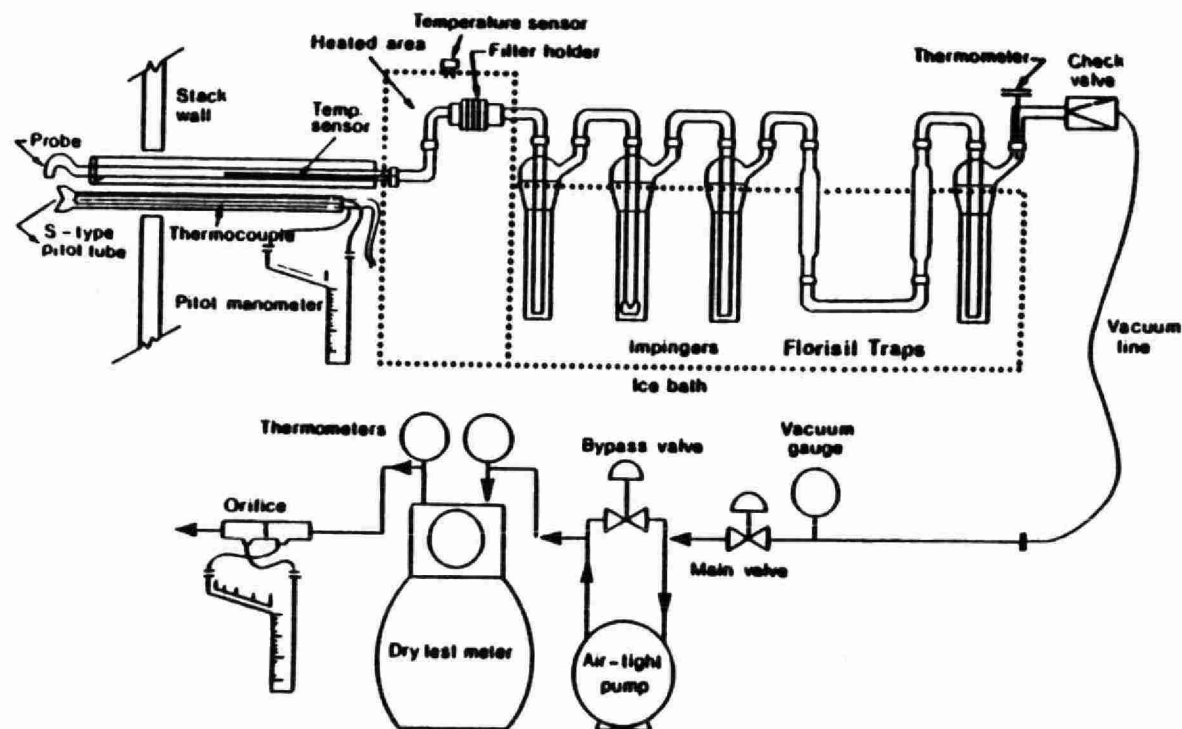
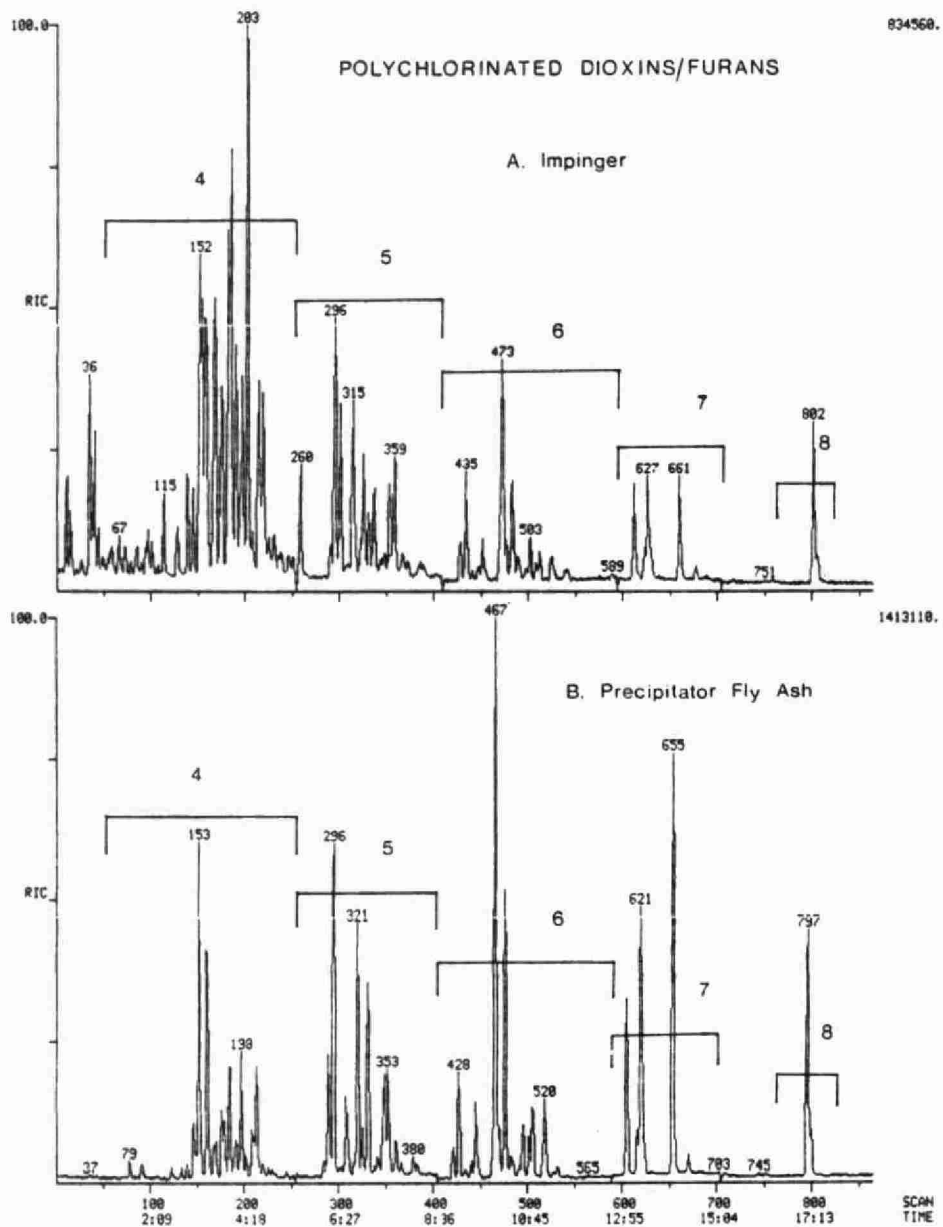


Figure 3 : Clement et al



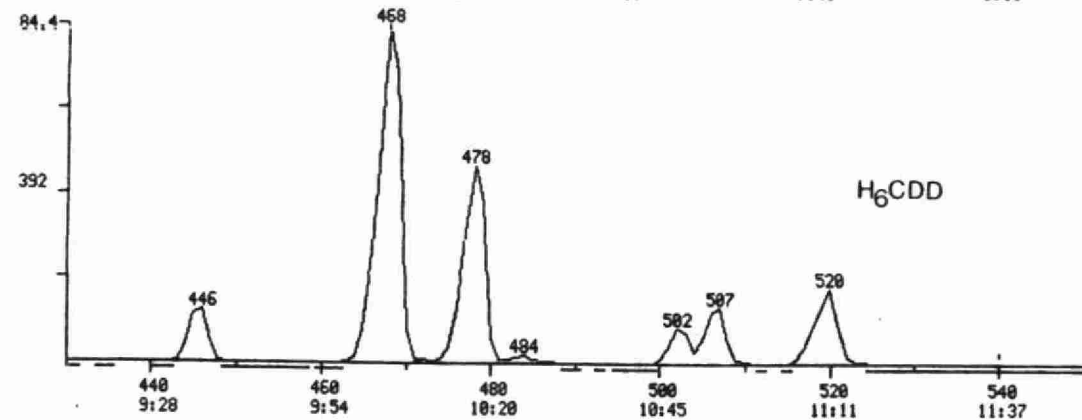
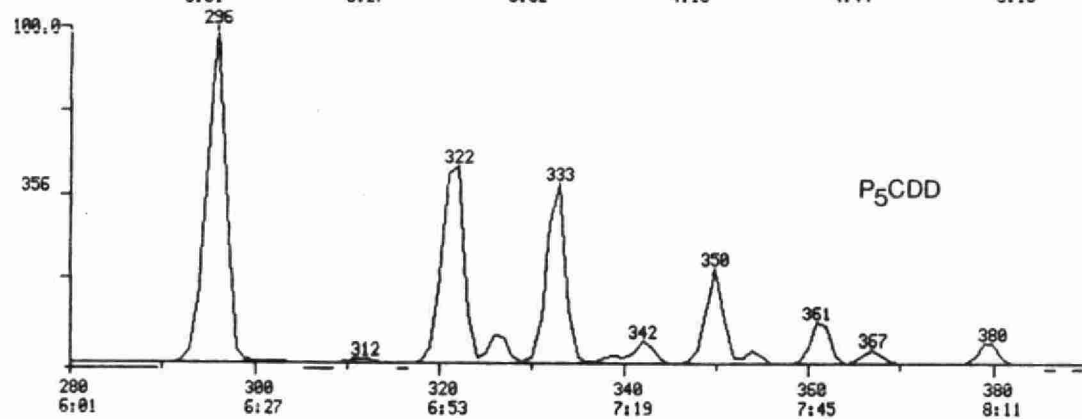
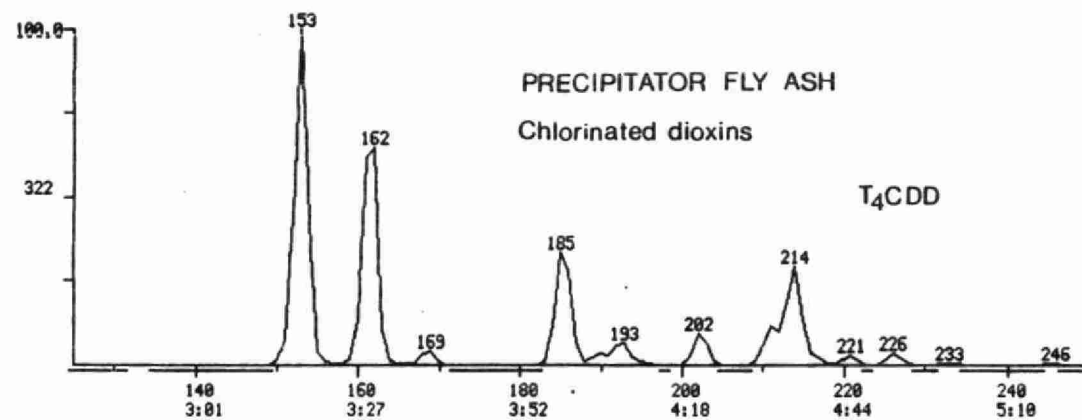


Figure 5: Clement et al

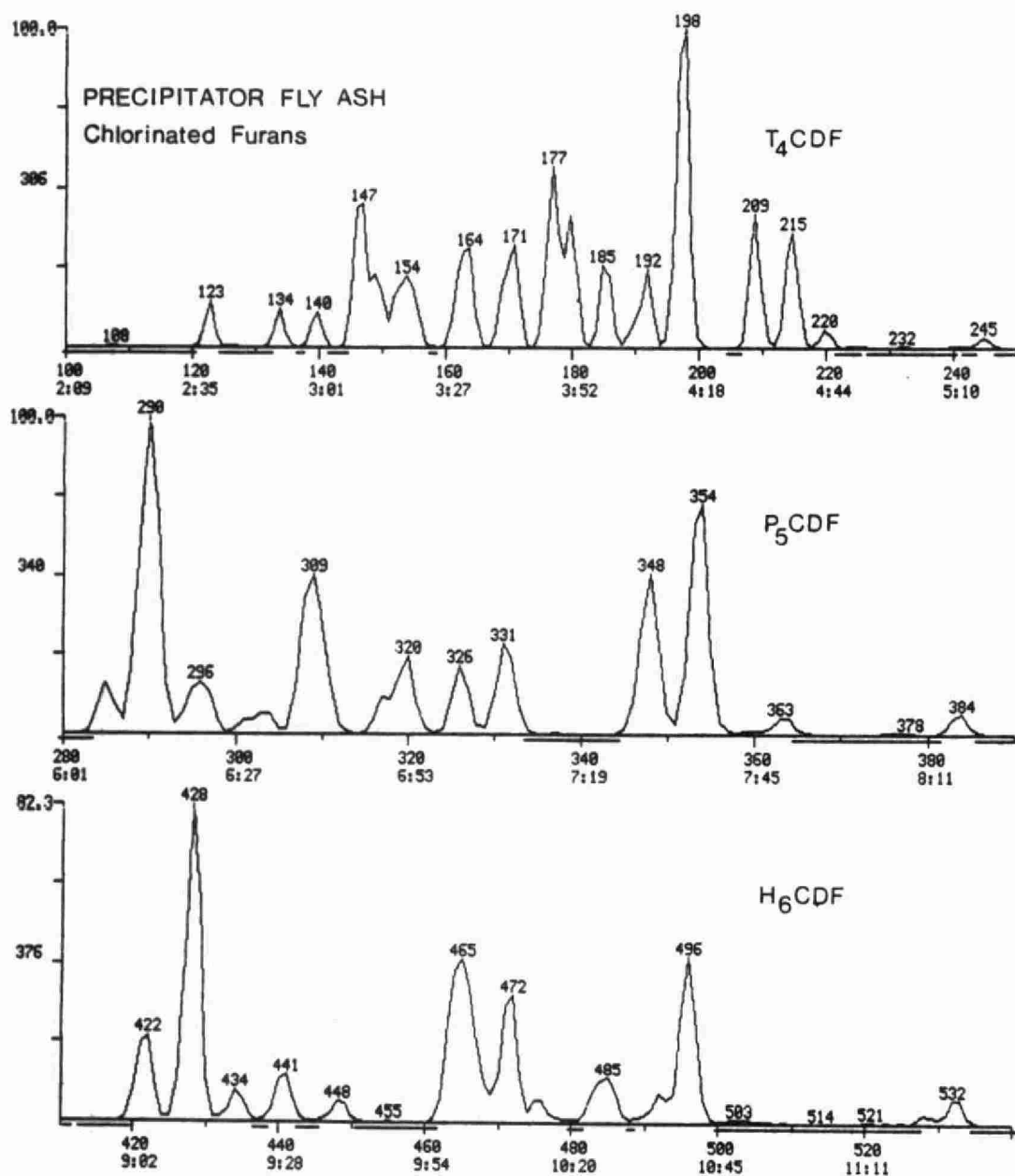


Figure 6: Clement et al

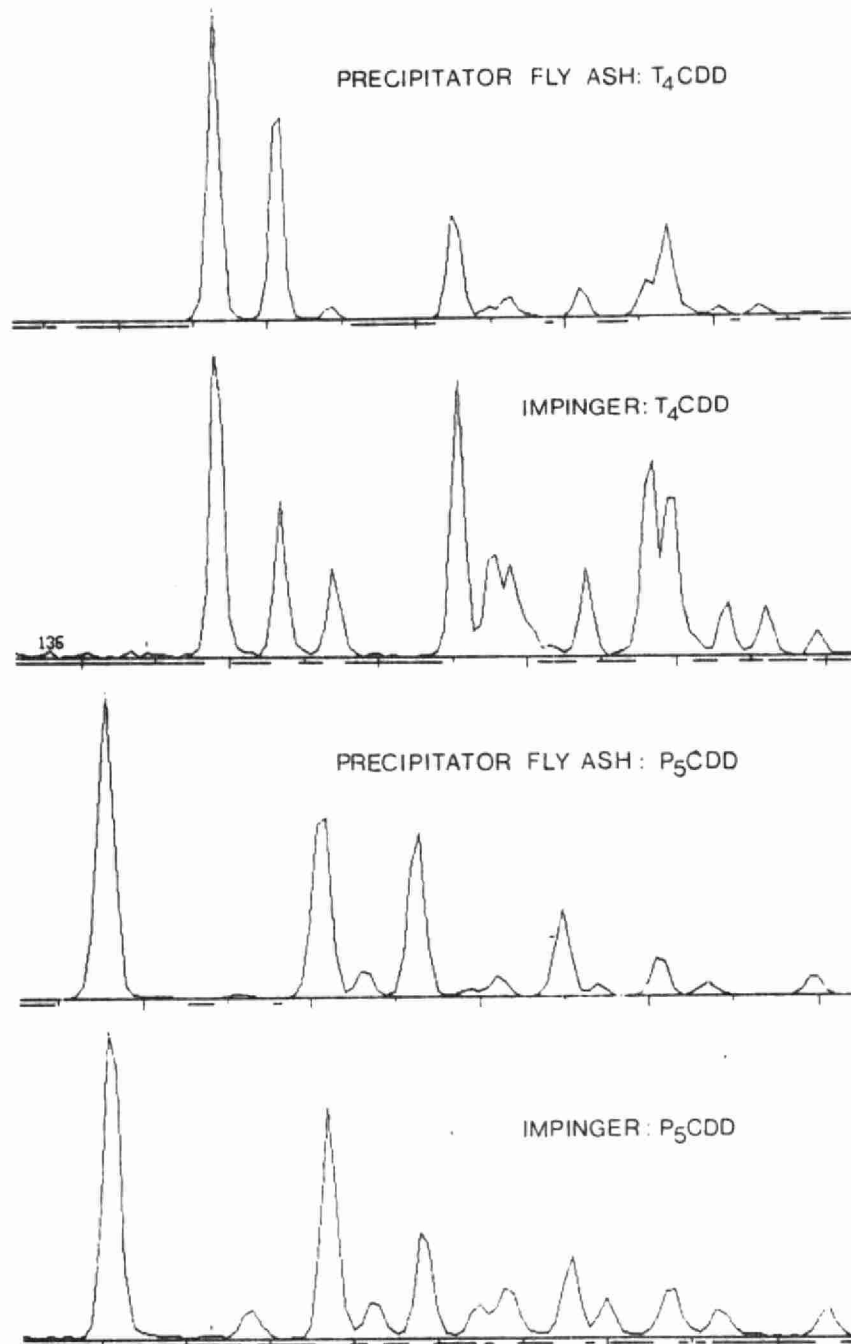
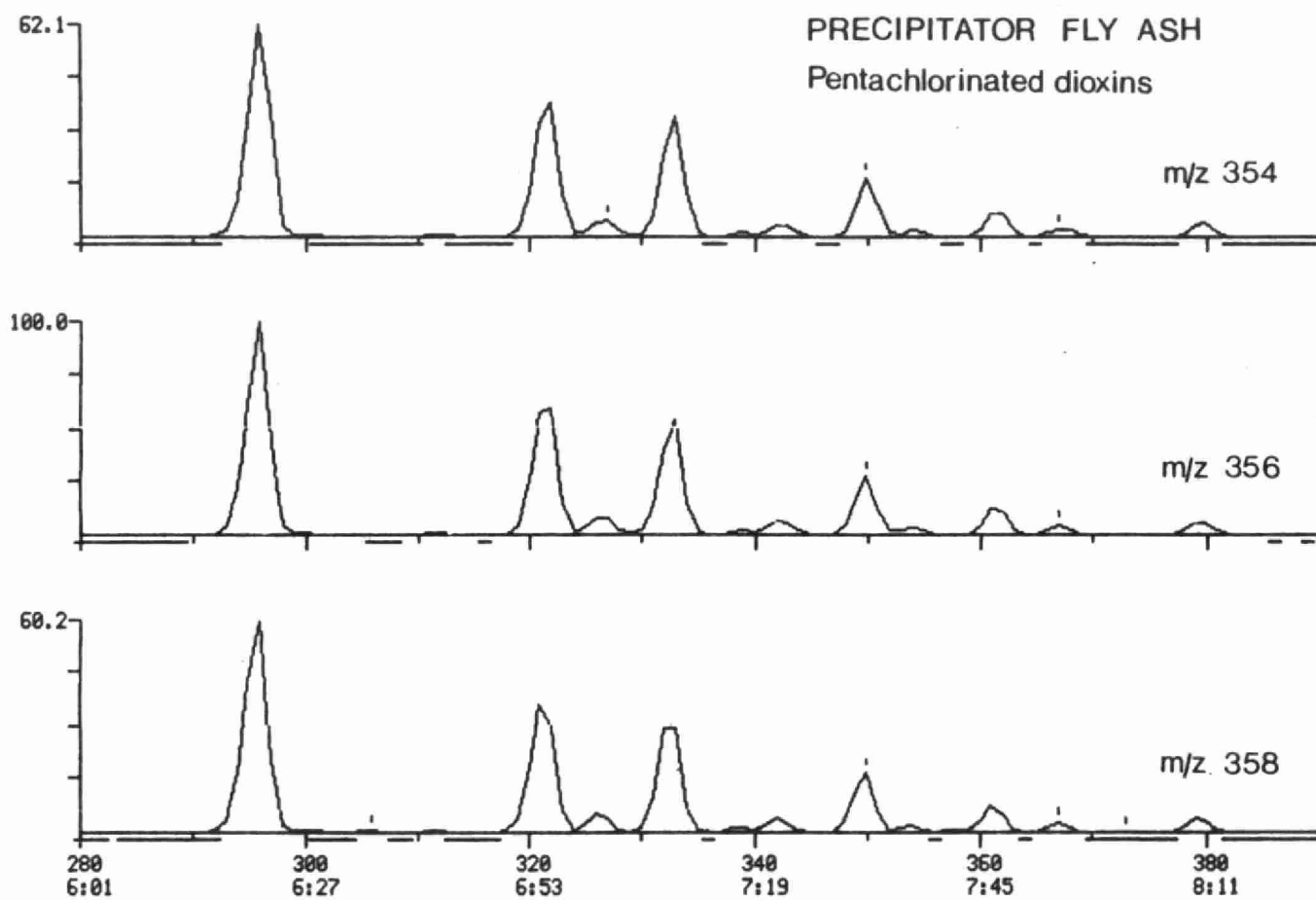


FIGURE 7: Clement et al.







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